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SAFETY ANALYSIS FOR NAVAL LIQUID OXYGEN LIFE SUPPORT SYSTEM

PREPARED FOR
THE U.S. NAVAL RESEARCH LABORATORY
WASHINGTON, D.C. 20375
UNDER CONTRACT NO.
N00014-81-C-2307

PREPARED BY

GEO-CENTERS, INC.
320 NEEDHAM STREET
NEWTON UPPER FALLS, MASSACHUSETTS 02164

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I. INTRODUCTION

All submarines require a self-contained life support system to allow prolonged submerged operations. Present submarine operating procedures employ either electrolysis or chlorate candles to generate oxygen. A potential alternative to these conventional systems is the cryogenic storage of liquid oxygen (LOX), which at atmospheric pressure and normal ambient temperatures evolves at a rate comparable to that required for life support on a submarine.

With no moving parts, compact storage of the liquid form and worldwide availability, a LOX system poses as a simple and efficient alternative. Much experience with small LOX systems exists with aircraft, where all high altitude fighters and transports are so equipped. The simplicity, light weight, and minimum volume have proven effective.

Further, a LOX system actually used underwater to provide breathing oxygen was developed by Airco Cryogenics of Irvine, CA under contract N00014-67-C-0095 S4607 for the Office of Naval Research.[1] The system was tested in 1967 60 feet under water in Sea Lab I - STEP at the United States Navy Mine Defense Laboratory (USN MDL) at Panama City, FL. That part of the system which supplied breathing oxygen operated successfully and it was concluded that for future operations involving relatively short-term storage (less than five months), liquid oxygen should be seriously considered. Particularly in view of the large scale commercial distribution system of oxygen, it is felt that cryogenic storage of the product would be practical for many land-based, shipboard, and submerged applications.

However, liquid oxygen (LOX) with a boiling point of −183°C poses potential hazards which must be considered prior to engineering development; the hazards include those associated with

(1) the intrinsic properties of liquid and gaseous oxygen, and

(2) the changes in the properties of materials subjected to the low temperature environment.

The purpose of this reported research has been twofold:

(1) Review from first principles the properties of liquid and gaseous oxygen in a submarine environment, and

(2) apply these principles to a candidate shipboard design.

In the storage and transfer of LOX, the safety objectives are to get the fluid to the use or storage point in a pure state, to effect any disposal in a safe manner, and to prevent any damage to the system. Since oxygen exists as a liquid only at temperatures considerably below ambient, normal storage must account for an unavoidable, inexhaustible heat input available from the environment. If the heat input to LOX is excessive, vaporization may occur with explosive rapidity. The same condition may result if the LOX is allowed to become superheated. Superheated liquid nitrogen has caused dewars to explode. Many materials, particularly hydrocarbons, may ignite or explode under conditions of mechanical shock in the presence of liquid or dense gaseous oxygen. Gaseous oxygen, or GOX in missile vernacular, is generally regarded as being more dangerous to handle than the liquid.

It has been observed that all explosions in LOX systems actually take place in the gaseous phase because:

(a) The rapid "boil-off" rate of LOX forms an oxygen-rich atmosphere above the surface of the liquid.

(b) Combustible materials do not always react spontaneously in LOX, but will either burn or explode if ignited in the gaseous oxygen atmosphere above the liquid.

(c) Few reactions take place at the temperature of LOX.

(d) Gaseous oxygen reacts more readily with metals than any other element except fluorine.

The primary hazards of interest in dealing with LOX are those associated with the response of the human body to the fluid and its vapors, and those associated with reactions between the fluid and its surroundings. The first includes frostbite, respiratory ailments, and chemical burns; the second, phase changes, low-temperature effects, ignition, and other hazards. To these hazards which are always associated with handling LOX, another exists when LOX is used for supplying breathing oxygen, namely the physiological effects of too much or too little oxygen.

No effort is made in this report to examine the complex question of material compatibility. An extensive body of literature exists on this subject which must be consulted when hardware design is begun. Also not considered are cleanliness and contamination standards. Existing military standards (MIL STD) are presumed appropriate and sufficient. Because this analysis was intended to be an independent and early look at potential safety problems, little interaction has taken place between this contractor and the system designers or their safety experts beyond the acquisition of general system configuration and operating parameters. For this reason, many of the concerns raised in this report may already have been addressed. Further, due to the limited scope of this study, those areas of safety which represent standard engineering practice have been discussed only in a general way. Lastly, because of the system symmetry, detailed analysis of the candidate system is carried out only for a single storage tank of a multi-tank design.

II. GENERIC ACCIDENT REVIEW

An analysis was conducted of 206 accidents involving liquid oxygen.[2] The results of this analysis are shown in figure 1. The total number of citations is 237 because some accidents were the result of multiple causes.

The largest single cause of accidents was system contamination by hydrocarbons. In many cases where contamination was not the primary accident cause, it was a contributing factor. The classical fuel in oxygen system explosions has been acetylene, which is very sparingly soluble and which has precipitated from solution where evaporation of liquid oxygen was taking place.

The next two categories, operator error and poor maintenance, are amenable to reduction through "*foolproof*" design, comprehensive and continuing training, and a genuine commitment to safety.

The large number of cases in the "unknown" category reflects the often catastrophic nature of a LOX accident in which most of the evidence is destroyed.

One potential problem area which turns out to be a rather minor concern is personnel injury due to contact with LOX. Because LOX in contact with a warm surface is subject to film boiling, heat transfer is relatively poor. A major international producer and handler of cryogenic fluids with over 30 years experience states "our personnel injury incidence from 'cold burns' has been practically nil.[3]"

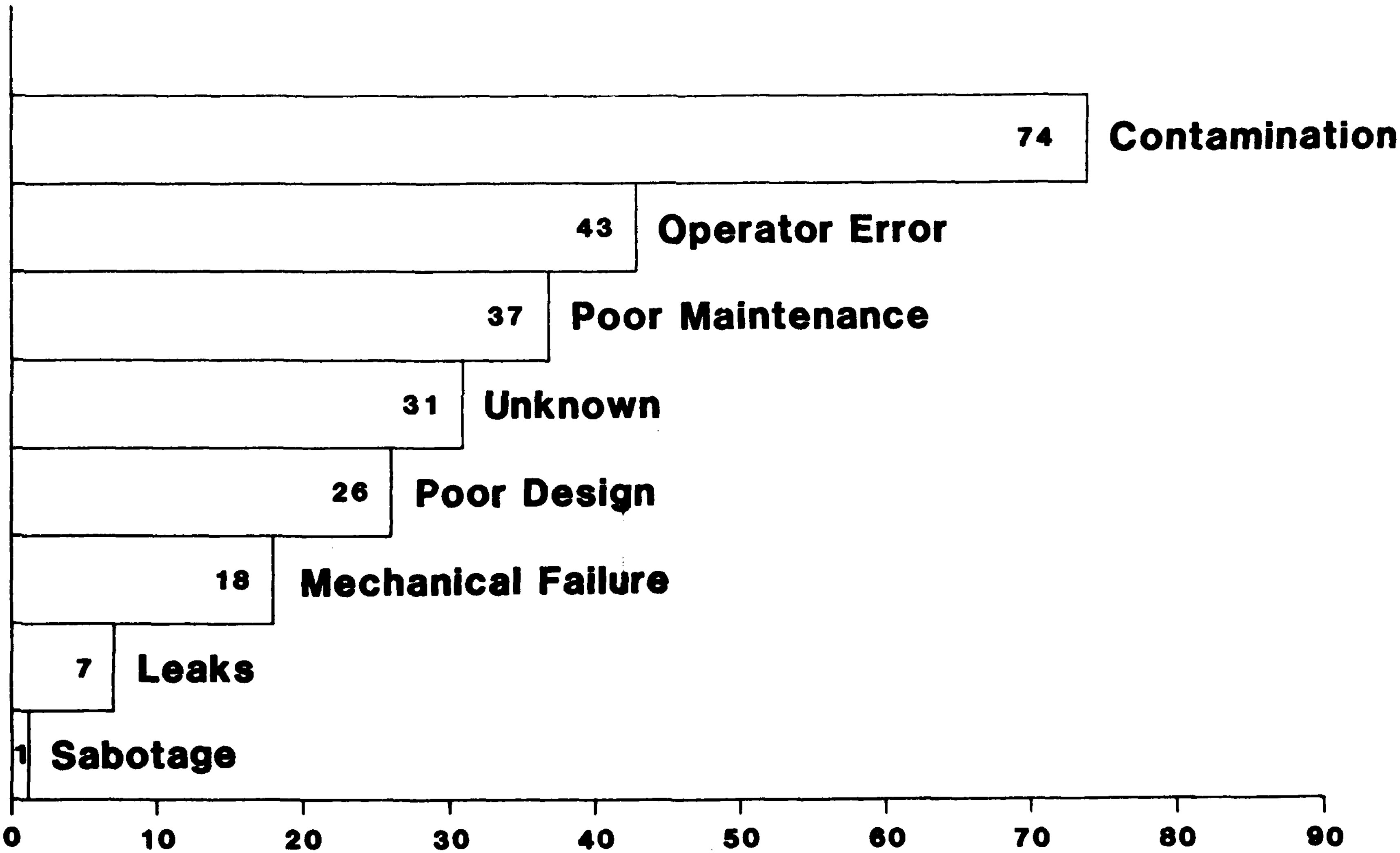

Figure 1. Accident causes in LOX systems - Summary of 206 accidents.

In the same study the following factors were found to be of primary importance in causing system failures in LOX facilities:

- Mechanical failure of the containment vessel, piping, or auxiliary components due to brittle failure or freeze-up.
- Reaction of the LOX with the confining vessel or auxiliary equipment.
- Reaction of the LOX with a contaminant.
- Failure of a safety device to operate properly.
- Operator error.

III. SYSTEM DESCRIPTION

A candidate liquid oxygen storage and supply system is shown in figures 2 and 3. Figure 2 shows that part of the system external to the pressure hull of the submarine. This includes all cryogenic parts as well as the fill and vent piping, vapor removal piping, rupture disks, and emergency vapor vent. Provision is made for transferring LOX from one tank to another as well as the emergency dumping of both liquid and vapor. The system is designed to be multiply redundant with similar piping configurations for all tanks. Each tank has a design volume of 70 ft^3 providing about 2500 man-days of gaseous oxygen per tank assuming a 10% ullage when full.

A 10% vapor space has been generally accepted as a standard condition, because it is difficult to fill a normal dewar to greater than 90% of its volume with rapid filling rates. At the end of most filling operations, inadequate cool-down of the dewar mass and a shallow de-entrainment space above the liquid will cause liquid to be carried into the vent piping. This indicates a full vessel, and at this point the vessel will be approximately 90% full.

Figure 3 shows the system internal to the pressure hull. The symmetry of the piping system allows vapor to be withdrawn from any tank and supplied to the submarine distribution system by any of several paths.

As designed, each tank would be filled separately. Using tank 1 as an example, the supply line would be connected at A, CV-13 and CV-11 would be opened while CV-12 and V-14 would be closed. LOX would be pumped until TC-11 indicated liquid in the vapor withdrawal line or the difference between PT-11 and PT-12 indicated the tank was full.

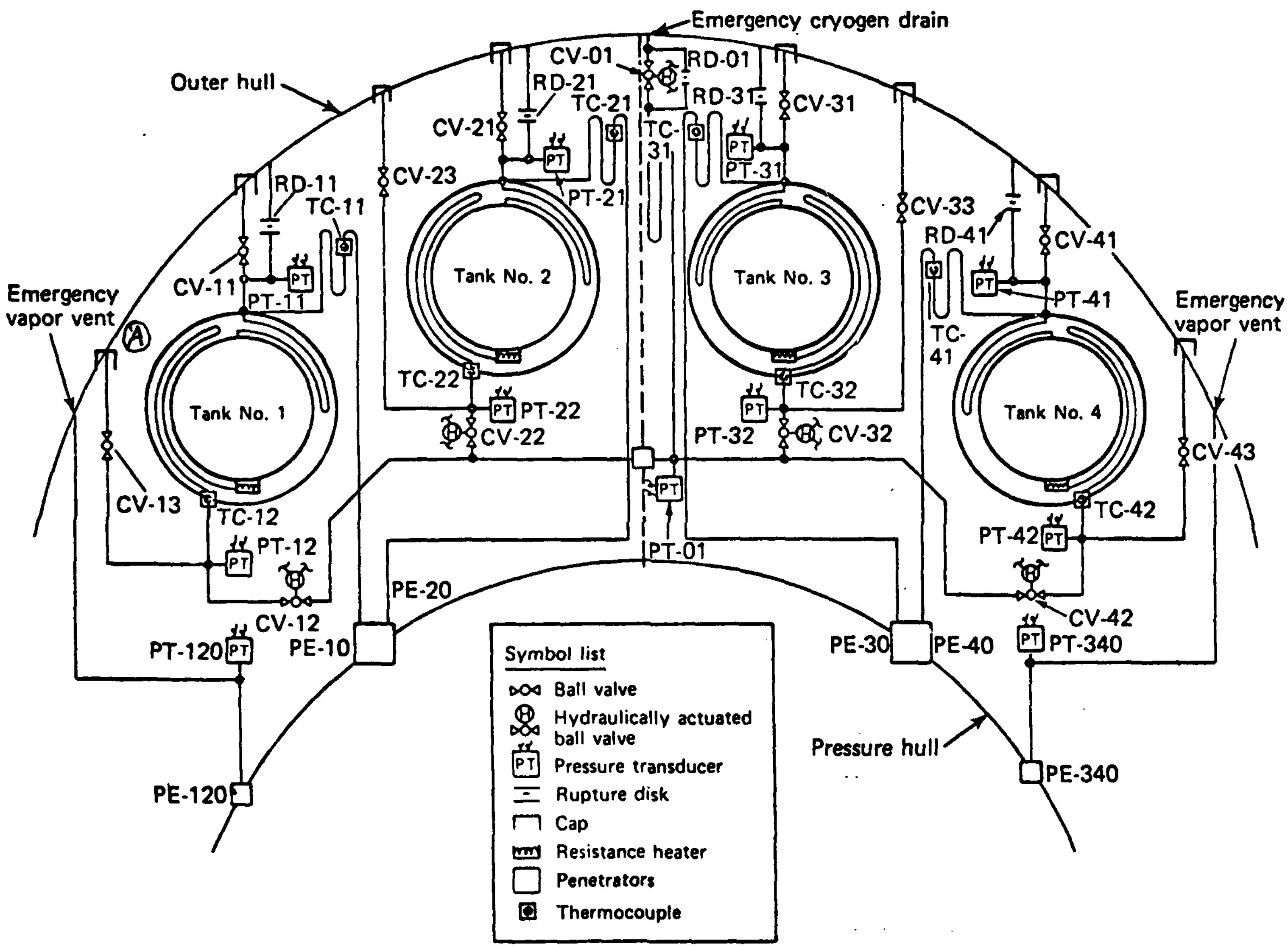

Figure 2. Inter-tank piping arrangement for the liquid oxygen storage system (schematic) (Annulus control system is not shown).

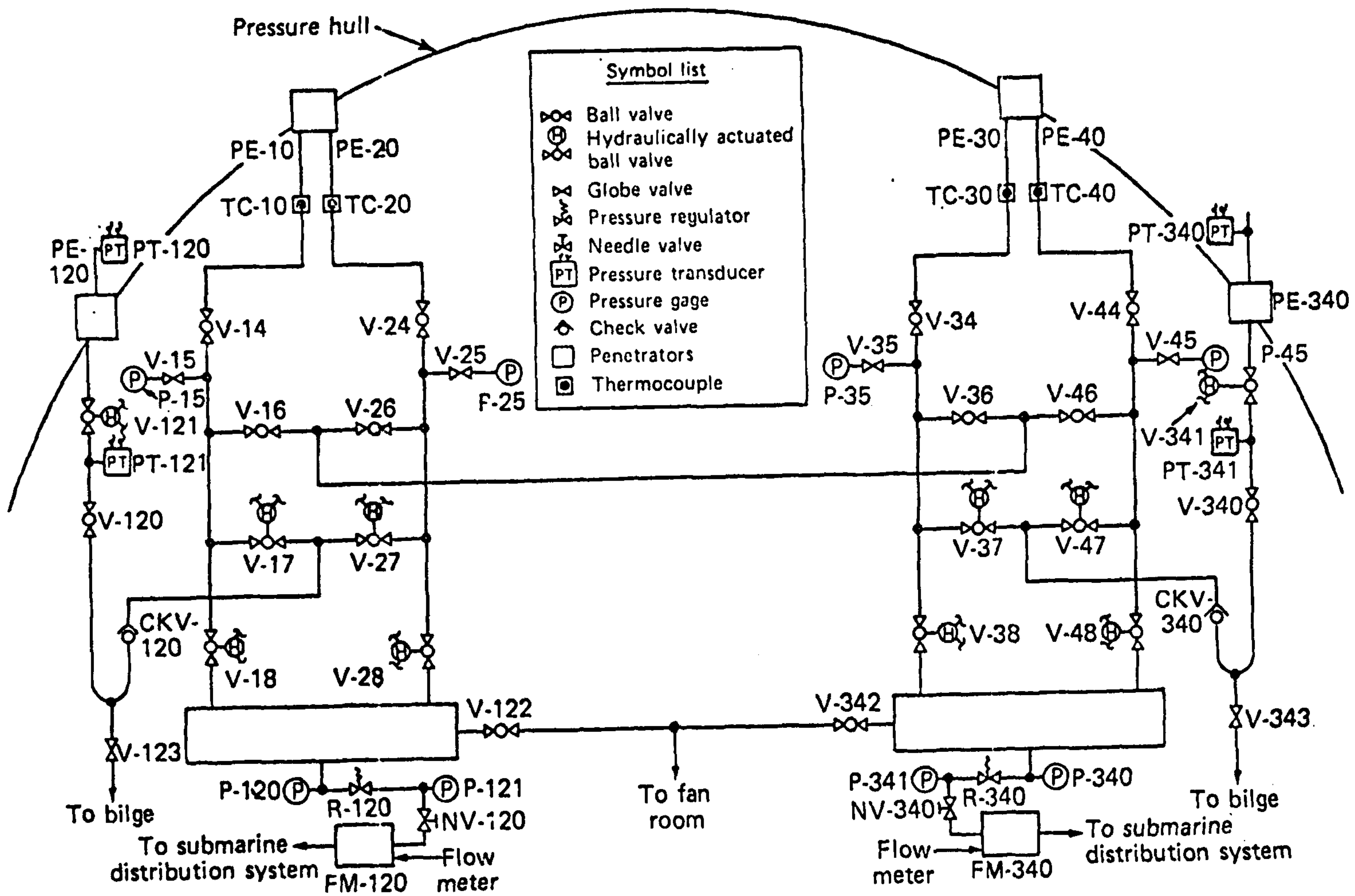

Figure 3. Oxygen flow control system (schematic).

At this time CV-13 would be closed and the supply line vented and disconnected. When TC-11 indicated that the vapor withdrawal line was free of liquid, CV-11 would be closed and V-14 could be opened admitting GOX to the distribution system.

When vaporization of LOX due to thermal in-leak is insufficient to provide the required flow rate, electrical heaters are provided on each tank to increase the vaporization rate as needed. Under normal operation, the entire system will be just sufficiently above atmospheric pressure to allow for pressure drops in piping, and other system components while providing for acceptable GOX flows.

The principal differences between this system and those which have been used routinely for many years are:

- All components of the system external to the pressure hull (including all cryogenic parts) must be designed to withstand sea water at the pressures encountered by the submarine.

- The system must be designed to withstand internal pressures sufficient to allow vapor venting or LOX dumping against the outside pressure encountered at depth.

- The LOX is not subcooled but is maintained at its boiling point.

It will be seen that the first two requirements present severe constraints on the system design.

Because of the requirement to be able to dump LOX while submerged, the inner vessel of the LOX storage tank must withstand a pressure greater than that of the surrounding sea water in order to provide the pressure differential necessary for dumping. Again using tank 1 as an example, the high pressure requirement extends at least to V-14 and for safety, probably should extend throughout the system.

IV. DESIGN SAFETY CONSIDERATIONS

IV-1. Pressure Vessel

Pressure vessels for storing cryogenic fluids including LOX are usually designed in accordance with the American Society of Mechanical Engineers (ASME) Code, Section VIII, Division 1; Code for Unfired Pressure Vessels. It should be noted, however, that the ASME code does not encompass baffle or internal piping designs, nor does it provide cleanliness specifications for oxygen service. The principal thrust of the code is the mechanical design of the pressure vessel shell and fittings.

Safe design requires the elimination of all pockets, crevices, or cavities in which accumulation of foreign matter could occur; all channels in which the reaction of foreign materials and oxygen could magnify the damage, and any piping in which the concentration of impurities or contaminants usually found in LOX could occur.

The low temperature of LOX can have a profound affect on the properties of the solid materials used in the containing system. The strength of materials is usually not a safety problem at LOX temperatures since strength increases as the temperature decreases. However, it is advisable to use room temperature strengths in the design of equipment for several reasons.

First, most proof testing is done at ambient temperatures; second, the equipment may warm up under stress; third, because of temperature gradients, not all of the system will always be at the system's lowest temperature.

The usual practice in cryogenic design calls for an inner vessel as thin as practical since a thick-walled vessel requires a longer time to cool down, wastes more fluid in cooldown, and introduces the possibility of thermal stresses in the vessel wall during cooldown.

Thermal stresses can arise during the cooldown of a system as well as during steady state operation. The physical properties which influence the magnitude of these stresses in a given material are the coefficient of thermal expansion, the thermal conductivity, and the elastic modulus.

In well insulated systems at operating temperature usually the only significant stress problems result from the axial thermal contraction of the cooled line. During cooldown, radial and circumferential stresses can also occur. Stresses due to transient gradients can be minimized by proper operating procedures.

Circumferential temperature gradients can result during the cooldown process from stratified flow in horizontal pipes which permits the bottom of the pipe to cool faster than the top. The differential thermal contraction will then cause the pipe to bow and the resulting stresses will depend upon the shape of the temperature gradient and the manner in which the pipe is restrained.

Because of the underwater venting requirement, the inner vessel of the storage tank must be designed to withstand full external ambient pressure. Operational restrictions will probably have to be put on filling rates to prevent severe thermal stresses in the wall. Long cooldown times are also anticipated. Thick walls on inner tanks are not unprecedented. Very large LOX storage tanks (900,000 gallons) have walls nearly 1.5" thick near the bottom to withstand the weight of the liquid.

The thermal capacity of most solid materials at low temperatures is very small because of the decrease in specific heat as the temperature decreases. For this reason, the solid material in a system is not effective in retarding a rapid temperature rise for a given heat input. In general the largest thermal capacity of a LOX system resides in the LOX itself.

IV-2. Contamination Control

As shown in Section II, the most frequent cause of LOX accidents is a chemical reaction between the LOX and contamination in the system.

For LOX systems where contamination can be hazardous, it is necessary to remove undesirable gases from the system by purging. For portions of the system with large length to diameter ratios ($L/D >> 1$) a flow-through purge is usually most effective. This portion of the system must be equipped with suitable purge-gas introduction and vent ports, a purge-gas supply system, and gas sample ports. A gas analysis capability should also be available. For components with small length to diameter ratios or in which the entire volume cannot be swept with purge gas, purging is effected by either evacuation and backfill to 1 atm or pressurization to a few atmospheres followed by venting to 1 atm. The previous steps or combinations thereof are repeated as required to obtain the desired purity. One should not rely upon computations or experience to determine the extent of purge effected. The inevitable existence of dead-ends, adsorbed gas, and incomplete mixing makes purging less than 100% effective even for simple systems. For this reason gas analysis is required for verification of purge adequacy. Also gas samples should be taken from locations where purging is least likely to be complete. Gas analysis is usually accomplished by means of a mass spectrometer or a gas chromatograph.

As an additional precaution in the long-term storage of LOX, periodic warm-up (defrost) and analysis of the dewar contents is desirable. Each warm-up should bring the coldest spot in the dewar to a high enough temperature that the most likely impurity is above its normal boiling point.

A purge system has been considered[4] which would tie into the proposed system at P-15 (see Figure 3). Any purge system should incorporate a check valve to keep oxygen out of the purge system unless the purge gas is oxygen.

A back-up GOX system, connected to the system at the purge point, V-15, might be a reasonable precaution. The GOX could also be used as the purge gas as is standard on aircraft.[5]

As the heavier hydrocarbons are only slightly soluble in LOX, it is most unlikely that dangerous concentrations ot these materials will be present. However, in a system subjected to normal storage and handling procedures, frozen, solid hydrocarbon particles can flake off and move with the liquid. If this debris lodges in a valve, a fire or explosion may result due to impact forces generated by opening and closing the component. It is also important to monitor for CO_2 because of possible clogging of components due to the presence of dry ice. Slight changes of tank temperature or pressure can cause precipitation or CO_2 in any LOX system in which the concentration has been observed to be at or above its saturation point.

Since LOX is continually boiling in the storage tanks, the composition of the fluid is continually changing, with CO_2 and nonvolatile materials concentrating and settling out in direct proportion to the evaporation rate. These contaminants will generally accumulate in the quiescent regions of a tank or system and are seldom uniformly distributed. Moreover, data accumulated at several government research centers show that CO_2 is present in all oxygen loading systems in excess of its saturation point; hence, in a solid state.[6] Because the density of CO_2 is greater than that of LOX, it sinks to the bottom of the tank and has actually been removed by hand shoveling. Even though CO_2 particles can clog a filter, the individual particles tend to migrate through, whatever their initial size, and no known LOX filter will hold back all of the CO_2 once it is in the system.

When impurities exceed their solubility and come out of solution, forming islands of solid within or on the surface of liquid oxygen, it is evident that localized flammable mixtures can occur even though the average concentration throughout the system may be far below the flammable range. Normal liquid sampling and analysis techniques (useful in safeguarding against more soluble hydrocarbons) are not capable of detecting the approach of insolubles to hazardous concentrations.

A special hazard exists in the proposed design because of the use of hydraulic valves in the LOX piping. Contamination of the LOX by hydraulic fluid must be absolutely prevented. In addition, the LOX must be thermally separated from the hydraulic fluid to prevent freeze up from interfering with valve actuation.

IV-3. Leakage

It is frequently difficult to prevent all leakage paths in a large and complicated system. For this reason, such systems are usually maintained at a pressure above ambient (usually 1 atmosphere air) so that if leakage occurs it will be out-leakage which is usually tolerable.

Any leakage into a cryogenic system can cause line blockage as a result of frozen vapor from H_2O or gases. Such frozen particles in a system can also be troublesome by causing valve seat erosion or by accumulating undesirable impurities. Such solid impurities do not necessarily leave the system with the LOX and thus can accumulate over a period of time. For this reason as well as the large liquid to vapor density ratio which proportionally increases any undesirable property of the LOX, such fluids have been referred to as risk concentrators. However, the degree or risk is usually less than that involved in the use of an equal quantity of high pressure gas. The surroundings of all LOX equipment including lines and valves must be scrutinized for possible hazards in case of LOX leakage out of the system.

Leakage in the proposed system could have particularly unfortunate results. While the submarine is submerged, any leakage of the system outside the pressure hull (which includes all cryogenic components) will be leakage of sea water into the system. Possible results of this in-leakage will be discussed in Section VII. A possible means of circumventing this problem would be to maintain the system at high pressure and provide pressure reduction inside the pressure hull. This would require only minor redesign since the system must be capable of withstanding high pressure to allow for underwater venting. The hazards associated with high pressure LOX storage would have to be carefully considered.

IV-4. Overpressure and Venting

All isolatable spaces which can hold LOX must be provided with some method to accommodate at safe pressure the maximum gas evolution rate that could occur. (This usually occurs upon the complete loss of insulating vacuum.)

When more than one valve is used in a given section of piping, a suitable pressure relieving device must be used in each section of piping between valves to protect the pipe from rupture in the event that both valves are closed with liquid in the pipe. Check valves can sometimes be used instead of manually operated valves, in which case the relieving device may be unnecessary.

The vacuum shell of cryogenic vessels should be equipped with a pressure-relief device to prevent overpressurization in the event of a leak from the inner shell into the vacuum space. If the relief device is a rupture disk, the disk should be supported with a vacuum backing disk. This will prevent collapse of the rupture disk when the insulation space is evacuated.

Vacuum-insulated lines should also be provided with relief devices for the annular space.

Rupture disks require time to operate and may not provide protection during very rapid pressure excursions, as, for instance, when a detonation occurs.

The rupture disks must be sized to handle either the maximum flow rate if the heater failed "on," the maximum fill rate if the vent valve were left closed, or the maximum gas evolution rate if all insulation were lost, whichever is greater.

Liquid containers are normally protected from overpressure by means of a standard safety valve. In this application, however, such a device may be subject to frost accumulation when in operation; and there is the possibility that it may subsequently freeze shut. Furthermore, the change in temperature may affect the valve spring constant and change the relieving pressure.

Because the rupture disks provide the only protection for the system from over pressure, their design must be carefully considered. Accommodation must be made for the large reaction force which could develop if a rupture disk bursts. Careful consideration should also be given to the thermodynamic situation which exists if a rupture disk bursts to ensure that any sudden gas evolution due to pressure release boiling can be accommodated.

The design of the vents for the rupture disks, as well as those for the cryogenic vapor vent and emergency cryogen drain, present a difficult problem. These must be somehow open to the environment and also provide personnel protection snould they release while the ship is on the surface.

Some means must also be provided to prevent the changing pressure on the outside of the rupture disk from changing the calibrated burst pressure of the device. A double disk with the outside disk calibrated to a lower burst pressure might be one solution.

Personnel protection is particularly important for the vapor vents, since cold GOX will be issuing from these during the filling operation while crewmen are on deck. Some sort of vent extender may be required for the filling operation. An extender would also allow the GOX to be vented away from the ship in a secure location.

During an underwater venting or LOX dump, some provision must be made to keep the vents from becoming plugged with frozen sea water. It has been suggested that this could be accomplished by either maintaining a high flow rate or providing electric heaters on the vents.[4]

Another method might be double valves in series. Sea water would keep the outer valve warm while the "dead space" between the valves could be heated, if necessary.

Some sort of experimental program to test the feasibility of underwater dumping of LOX will probably be necessary. It is to be noted that if the rupture disk bursts underwater, the entire system at least up to V-14 will fill with sea water. Even for controlled dumping or venting through CV-01, some sort of check valve to prevent sea water ingress will probably be necessary; otherwise, very close attention will have to be paid to pressure differentials between the system and the environment. The emergency vapor vent almost certainly needs a check valve, for without it, there will be sea water at full pressure all the way to V-121, inside the pressure hull.

Following a tank to tank transfer of LOX, some liquid will inevitably remain in the transfer line. This liquid will vaporize leading to high pressures. Venting to a selected tank, while possible, requires careful control of the pressure differential to prevent equilibration followed by a flow of LOX back into the transfer line. This problem would be obviated if the suggested check valve were installed in the emergency drain line. CV-01 could then be opened and the over pressure vented through the emergency drain line until PT-01 indicated a return to safe pressure.

IV-5. Ignition Hazards

Most fuel-oxidant mixtures will not spontaneously react when placed in contact. The activation energy for initiation of the reaction must be supplied in order for combustion to proceed. As an important part of hazard control, the forces which initiate combustion must be recognized and avoided, but this should be the second line of defense, not a primary one. Modes of ignition include:

(a) Discharge of static electricity from suspended particles to vessel walls.
(b) Shock waves in gases, liquids, or solids.
(c) Adiabatic compression of gas bubbles in liquids.
(d) Chemical reactions leading to formation of sensitive chemical compounds.
(e) Trace amounts of catalytic or reaction promoting materials.
(f) Trace amounts of unstable materials which may decompose to release heat.
(g) Mechanical energy input through fluid flow, action of valves, or devices which may introduce frictional heat or shock energy.
(h) Energy input through the kinetic energy of transported solids.
(i) Erosion of surfaces leading to accelerated chemical reaction.

All equipment containing LOX or GOX, including fill lines and vent lines, should be grounded. In transfer operations grounding all equipment to a common potential is important. Static protection is not now required when tank cars, tank vehicles, or marine equipment are loaded or unloaded by conductive or nonconductive hose, flexible metallic tubing, or pipe connections through or from tight (top or bottom) outlets because no gap exists over which a spark can occur.[7]

High humidity makes a contribution to safety in avoiding static sparking by improving conductivity in the environment; relative humidity over 70% is particularly effective in preventing buildup of static charges.[8]

IV-6. Instrumentation

A valuable and necessary adjunct to any transfer and/or storage system is adequate instrumentation. The requirements include:

(a) Pressure measurements in storage spaces, insulation spaces (vacuum) and in the transfer lines.

(b) Temperature measurements in the storage space (to facilitate warm-up analysis).

(c) Liquid level measurements in storage dewars.

(d) Flow measurements on both the liquid and purge systems (to provide reproducible purge flows).

The system as designed shows no way to monitor flow through any of the vent lines. Other instrumentation which might be considered includes an oxygen monitor in the ballast hull for an indication of leakage and a low pressure alarm to indicate major system failure. An excess flow shutoff valve could help ameliorate the effects of a major leak.

IV-7. Miscellaneous Design Features

In providing a system to store and transfer large quantities of LOX, the designer must pay strict attention to fluid velocities and to the phenomena which occur at the liquid-vapor interface. The dynamic forces involved when this interface is disturbed as well as vessel block valves and downstream piping should be analyzed to determine if their configuration will contribute to "water hammer." Lines and vessels containing LOX should be plainly marked for easy identification. Systems intended for military use must not shatter when pierced by gunfire, and to this end, they are sometimes bound with wire or steel cables.

V. OPERATIONAL SAFETY CONSIDERATIONS

First indication of a system malfunction is often a high boil-off rate or patches of external frost. Especially during the filling operation, crewmen should be instructed to watch for these signs. The filling hose should always be disconnected immediately after the vessel is filled. Otherwise, since some liquid is trapped in the hose, it will continue to evaporate, and the hose might rupture as a result of the pressure buildup.

Localized extremely high temperatures may be obtained through the adiabatic compression of a gaseous bubble confined within a liquid system. Hydraulic shock waves may result in compression of the bubble for an instant of time to extremely high pressures and the attendant very high adiabatic compression temperatures. Such bubble compression is well known as a source of initation of flammable mixtures since the bubble and the flammable mixture immediately associated with it may be well above the combustion temperature. Any intentional pressurization of the cryogenic portion of the system must be done slowly enough to avoid this potential hazard.

Filling the LOX tanks must be done very slowly for at least two reasons.

(1) Because of the unusual thickness of the inner vessel, radial and circumferential thermal stresses can become quite large.

(2) As the tank approaches full, liquid will tend to percolate into the vapor withdrawal line giving transient low temperature readings at TC-11.

When transferring liquid oxygen, do not leave valves open all the way; open them wide and then immediately close them about one-quarter turn; otherwise, they may freeze in the open position.[3]

VI. FAILURE ANALYSIS

Except for instrumentation, the system would not be seriously affected by a loss or electric power.

A failure of the hydraulic system would be much more severe. Without hydraulic pressure, there is no way to either dump or vent unless the hydraulic valves, e.g. V-17 and V-121, can be operated manually. Even with loss of hydraulics, the system is still protected by the rupture disks. It should be noted that because the liquid is at its saturation point, any reduction in pressure will lead to a very rapid gas evolution as the liquid returns to saturation at the new pressure. Any failure of lines or tanks would involve leakage and is discussed in Section VII. A Failure Analysis Listing for critical valves and vents is shown in Table I.

Table 1. Failure Analysis Listing for Critical Components of Candidate LOX System

Valve	Failed Open	Failed Closed
CV-11	Protected by deck cap	Unable to vent during filling of tank 1
CV-12	Unable to isolate tank 1	Unable to dump LOX in tank 1 or transfer tank 1 contents
CV-13	Protected by deck cap	Unable to fill tank 1
V-14	Redundant	Must transfer contents to another tank to utilize
V-15	Purge system always under pressure	Must open V-16, 26, and 25 to purge
V-16	Redundant	Redundant
V-17	Redundant	Redundant
V-18	Redundant	Redundant
V-123	Must vent through V-340	Must vent to bilge through V-343
V-120	Redundant	Must vent through V-340
V-121	Redundant	Must vent through V-341
CV-01	If there is no check valve, water enters LOX transfer line preventing tank to tank transfer and emergency dumping	Can't dump LOX
Heater	Must transfer LOX to another tank and or vent excess vapor	LOX may be transferred to another tank if necessary

Failure analysis indicates three situations of possible concern:

1. If CV-12 were to fail closed, it would be impossible to either dump the contents of tank 1 or transfer its contents to other tanks. Should an emergency arise, the LOX could be vented as a vapor through the emergency vapor vent. Should the gas evolution rate be too great to be accommodated, the system would still be protected by the tank 1 rupture disk.

2. If CV-01 failed open, sea water would enter the LOX transfer line (in the absence of a check valve). Subsequent attempts at either tank to tank transfers or cryogen dumping might cause the water to freeze, plugging and perhaps rupturing the line. Each individual tank would stil be protected by its own rupture disk.

3. If CV-01 failed closed, emergency dumping of LOX would be impossible. The system would still be protected by rupture disk RD-01.

VII. LEAKAGE CONSEQUENCES

VII-1. Pressure Vessel

The consequences of an insulation vacuum leak in a LOX storage tank are difficult to analyze because of the highly nonequilibrium situation which would exist. The worst case (and probably the most likely) would be for a leak to develop while the vessel was deeply submerged. This would be most likely because the pressure differential would then be greatest. Two cases exist; namely:

(1) A leak through the inner vessel

(2) A leak through the outer vessel.

For an inner vessel leak, the insulation space would begin to fill with LOX which would quickly vaporize, resulting in a large over pressure causing the insulation space rupture disk to burst, followed by an in-rush of sea water.

For an outer vessel leak, the insulating space would immediately fill with water. In either case, as the water cooled it would begin to freeze. Since the thermal conductivity of ice is about 20 times smaller than steel, the ice would serve to insulate the inner vessel. Note however that ice is a better heat conductor than water by almost a factor of 5.

As ice cools from 0°C to LOX temperatures the specific heat decreases by a factor of 5 making it less able to retard temperature changes. In addition, as the water freezes, it expands by about 10% causing tremendous stress on both the inner and outer vessels.

Meanwhile, the pressure in the tank has been increasing due to the thermal vaporization of the LOX and will necessitate transferring the remaining LOX to other tanks (if space is available) or dumping. If the leak has been in the inner vessel, some sea water may be in the LOX tank but as ice (or water for that matter) is lighter than LOX, it should float and not block the liquid drain at the bottom.

VII-2. LOX Fill Line

A leak of sea water into the inner section of the fill line inboard of CV-13 would probably be detectable as an increase in PT-12 due to vapor evolution as the sea water contacted the LOX. This increase might not be very great for two reasons. First, tank 1 would act as a buffer, absorbing some of the excess pressure. Second, the water would freeze forming an ice plug insulating the LOX to some extent and blocking the entry of more water unless the phase change expansion caused the pipe to burst. Should this happen, the sequence would be repeated until the tank was reached at which point the analysis proceeds as in the case of a pressure vessel inner shell leak.

A leak of sea water into the insulating space on this line would be detected as a pressure increase on PT-12. How this could be distinguished from the previous case is not clear. How much heat was transferred to tank 1 would depend on the piping geometry. If two phase flow could occur with LOX flowing out to the warm section on the bottom of the pipe and returning along the top as vapor, the heat transfer could be relatively efficient. If, however, the vapor were trapped, heat transfer would not be nearly as great. A transfer or dump could probably still be effected in either case.

VII-3. LOX Transfer Line and Emergency Cryogen Drain

Sea water leaking into the LOX transfer line would be detected by a pressure rise on PT-01. Should personnel interpret this as trapped LOX vaporizing and attempt to relieve the pressure by opening CV-12, a hazardous situation would exist. Opening CV-12 or any subsequent attempt to use the line for tank to tank transfer or emergency cryogen dumping would cause the water to freeze, creating an ice plug which could burst the pipe.

Should sea water leak into the insulation space of this line, the leak would probably not be noticed unless and until the line were used for tank to tank transfer or LOX dumping. When CV-12 was opened, the LOX would vaporize rapidly, causing a rapid pressure rise at PT-01. Problems similar to those encountered for a vacuum leak on a tank would occur, i.e. the water freezes in the vacuum space and threatens to burst the line. A transfer or dump might still be accomplished if done quickly enough.

VII-4. GOX Supply Line

Sea water leaking into the GOX supply line would flow into the inner vessel of the LOX tank. This would first be observed as a rapid pressure rise in PT-11. The heat given up as the water froze in the LOX tank would cause rapid evolution of vapor. Since the ice is lighter than LOX, it would float, perhaps making it possible to transfer the LOX to another tank.

VII-5. Vent Line

A leak in this line inboard of CV-11 would have the same effect as a leak in the supply line analyzed in VII-4.

VII-6. Emergency Vapor Vent Line

Without a check valve, sea water would already fill this line. With a check valve, sea water leaking in would fill the line to V-121. This would be detected by a rapid pressure rise at PT-120. Venting could be done as usual with the operational limitation that before V-121 is opened, PT-121 must read a higher pressure than PT-120.

VII-7. Internal Piping

A leak inside the pressure hull would be a leak of GOX at low pressure out of the system. This would be detected by a pressure drop at P-15 if the leak were of substantial size. An area oxygen monitor might be considered to provide an early indication of leaks.

VIII. SUMMARY AND CONCLUSIONS

This research effort has examined both the generic hazards of the use of liquid oxygen (LOX) in a closed (submarine) environment and specific concerns relative to a current candidate design.

In the generic analysis, more than 200 accidents involving LOX were investigated, and a chart showing the distribution of identifiable cases is shown in figure 1. This analysis identified the four most common causes, in descending order of frequency, as follows:

(1) Contamination of LOX system with hydrocarbons.
(2) Operator error.
(3) Improper maintenance.
(4) Unknown.

The large number of cases in the unknown category reflects the often catastrophic nature of a LOX accident in which much of the evidence is destroyed.

A similar analysis, conducted by Zabetakis,[3] identified a similar array of causes:

(1) Mechanical failure of cryogenic components due to low temperature fatigue or component freeze-up.

(2) Reaction of LOX with the containment vessel or auxiliary equipment.

(3) Reaction of LOX with a contaminant.

(4) Failure of safety devices.

(5) Operator error.

With this background, a specific system currently under consideration by the Navy was examined to identify possible areas of concern. Since this critique was conducted independent of the designers, many of these concerns may already be addressed. Details of individual system component analysis is given in the body of this report; only the major points are summarized here:

Hydrocarbon Contamination: Sources of contamination include: intrinsic LOX contamination, filling procedures, leakage, and hydraulic fluids from valves and pumps. Suitable standards and procedures can minimize the rate of contamination through handling channels; isolation of hydraulic systems from LOX can eliminate this channel; periodic purging can eliminate contaminant build-up; and instrumentation can be utilized to monitor contamination level. This latter point is important since most hydrocarbon contaminants are relatively insoluble in LOX; they will precipitate out and not be uniformly distributed throughout the system. Suitable monitors, particularly at accumulation points, e.g. valves and stagnant portions of the system, should be installed. Routine sampling and purge procedures will likely be inadequate, since contaminants are prone to concentrate in stagnant portions of the system.

In addition to hydrocarbon contamination, the presence of water (H_2O) and carbon dioxide (CO_2) represents an area of concern since both materials freeze and become potential sources of blockage, stress (due to the thermal expansion of ice), pressure build-up, and eventual rupture. Many of the hydrocarbon contaminants, as well as the CO_2, can be eliminated by periodic warm-up of the system to boil them off.

Leakage: Depending upon pressurization there can be leakage either into or out of the cryogenic system. Inward leakage is considered the more hazardous situation; therefore it is recommended that consideration be given to a LOX system pressurized to maintain positive pressure, even at depth. The major concern is that inward leakage leads to contamination either by hydrocarbons or sea water, the hazards of which have been discussed. There is particular concern for the proper interpretation of data from status monitors. Examples have been cited whereby improper corrective action can catastrophically aggravate failure situations. It is strongly recommended that full-scale underwater system tests be conducted to evaluate the severity of various system failures.

Overpressure and Venting Since various parts of the cryogenic system must operate at vacuum, others at gaseous oxygen pressures, and still others at underwater pressures, there exists a great range of both positive and negative pressures. Under various mechanical failures, many of the components must be designed to handle both extremes. A series of check valves, rupture disks, and double valve disk arrangements has been discussed. For example, in the situation calling for the underwater dumping of LOX it is to be noted that if the rupture disk bursts underwater, the entire system at least up to V-14 will fill with sea water. Even for controlled dumping or venting through CV-01, some sort of check valve to prevent sea water ingress will probably be necessary; otherwise, very close attention will have to be paid to pressure differentials between the system and the environment. The emergency vapor vent almost certainly needs a check valve, for without it, there will be sea water at full pressure all the way to V-121, inside the pressure hull. Again, full-scale underwater system tests are recommended to simulate this and other accident scenarios.

Operations: A set of carefully adhered to operational standards must be developed to preclude damaging the cryogenic system, to identify potential problems, and to initiate proper corrective action. Among the major identifiable procedures are included: the slow filling with LOX to minimize thermal shocks, mechanical stresses, and heating of gas bubbles; constant inspection of external components for frost or other signs of leakage; and careful monitoring of instruments; e.g. computer-based monitoring, to ensure unambiguous interpretation. It should be repeated that improper corrective action, instigated by incomplete or improper readings, can aggravate rather than correct a problem. A correct and complete data set, however, should yield an unambiguous picture of the situation.

Should there be a loss of power, the major concerns are the possible loss of instrumentation and loss of automatic operation of the hydraulic systems. Temporary loss of instrumentation would be of major concern only under accident conditions; loss of hydraulic control would represent a dangerous situation, which can be obviated by manual hydraulic capability.

Miscellany: Basic instrumentation is needed to monitor fundamental parameters such as temperature, pressure, liquid level and flow rates. For example, the system as currently designed shows no way to monitor flow through any of the vent lines. More sophisticated measurement methods are needed to detect more subtle properties such as the presence of dangerous contaminants.

Interestingly, potentially hazardous contaminants will not generally ignite spontaneously, particularly at low temperatures; energy input would likely be required. Care is therefore required to minimize energy sources such as sparks and hot spots.

A Failure Analysis chart showing the consequences of the failure of critical valves in either the "open" or "closed" positions is shown in Table I.

Because of the many variables associated with the LOX concept of providing life support oxygen in submarine use, the general areas of concern identified in this and other safety related studies must ultimately be addressed in a field experiment that permits the simulation of various accident scenarios. The experiments should be performed at depths which simulate deep submerged conditions, since a most critical problem is the intrusion of sea water into the cryogenic system.

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